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CArbon-14 Source Term
CAST

Definition of operating conditions and presentation of the leaching experiments (D3.2)

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CAST – Project Overview

The CAST project (CArbon-14 Source Term) aims to develop understanding of the potential release mechanisms of carbon-14 from radioactive waste materials under conditions relevant to waste packaging and disposal to underground geological disposal facilities. The project focuses on the release of carbon-14 as dissolved and gaseous species from irradiated metals (steels, Zircaloys), irradiated graphite and from ion-exchange materials as dissolved and gaseous species.

The CAST consortium brings together 33 partners with a range of skills and competencies in the management of radioactive wastes containing carbon-14, geological disposal research, safety case development and experimental work on gas generation. The consortium consists of national waste management organisations, research institutes, universities and commercial organisations.

The objectives of the CAST project are to gain new scientific understanding of the rate of release of carbon-14 from the corrosion and leaching of irradiated steels and Zircaloys and from the leaching of ion-exchange resins and irradiated graphites under geological disposal conditions, its speciation and how these relate to carbon-14 inventory and aqueous conditions. These results will be evaluated in the context of national safety assessments and disseminated to interested stakeholders. The new understanding should be of relevance to national safety assessment stakeholders and will also provide an opportunity for training for early career researchers.

For more information, please visit the CAST website at:
http://www.projectcast.eu

CAST		
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Document title
Definition of operating conditions and presentation of the leaching experiments

Executive Summary

Task 3.3 will characterize ^{14}C release from irradiated Zr fuel cladding wastes sampled from different reactors: PWR, BWR and CANDU. Five partners are involved in the realization of experiments under conditions relevant to deep geological disposal (i.e. cementitious or argillaceous media): CEA (4), INR (7), SCK-CEN (10), RWMC (13) and JRC-ITU (15).

Two types of Zr wastes will be studied (Zircaloy-4 and zirconium-niobium M5 alloys) under a range of conditions (aerobic and anaerobic, argillaceous and cementitious water chemistries).

This deliverable reports the Zr fuel cladding samples that are available for the CAST project. The experimental design and working conditions for leaching and corrosion tests are also described.

Contents

1 Definition of operating conditions and presentation of the experiments at CEA

1.1 PWR cladding characteristics

AREVA will supply samples to CEA for use in WP3. The samples of fuel rods used in this study were discharged from PWR reactors and had an industrial treatment in AREVA-La Hague (Figure 1) :

- Feeding and checking

Once the cooling down period in the pool is over, the fuel element is transferred to R1 and T1 units. There, its identity and combustion rate are established before shearing.

- Shearing

Fuel is cut into lengths of approximately 35 mm. These “hulls” contain the nuclear matter. Gravity makes them fall into a 12-scoop dissolution wheel. Top and bottom end-pieces are handled separately: they are transferred to the end piece rinsers. Hulls and fine particles of Zircaloy are generated by the shearing of the cladding. After the shear operation, the industrial hulls have various geometries and sometimes they deviate from cylindrical rods. The hulls are crushed or distorted claddings with shredded ends and a matt appearance. Some empty shells are observed that have ruptured along their length in the transverse direction.

- Dissolution

The nuclear matter contained in the hulls of the fuel pins is dissolved in boiling concentrated nitric acid. Metallic structures withstand this chemical treatment and the hull pieces are removed using a bucket wheel and sent to a conditioning unit. The solution overflows towards the clarification unit. The Zircaloy-based hulls are transferred to the hull rinsers.

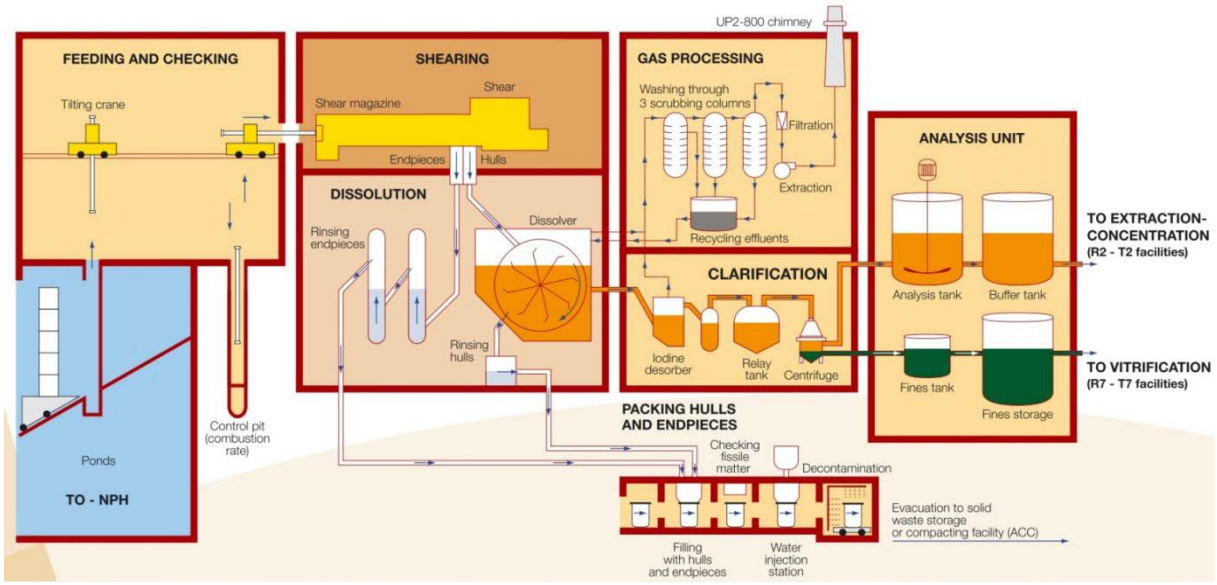

Figure 1 : Processing of the structural waste (hulls and end-pieces) in AREVA La Hague.

The hulls devoted to leaching experiments are currently stored in the hot laboratory ATALANTE (CEA) in Marcoule. We chose (approximately) cylindrically shaped pieces of claddings by remote operation. The flattened hulls were discarded to maximize the surface/volume ratio for the leaching experiments. The original diameter of the cladding was 9.5 mm and the thickness was 0.57 mm, with a length of about 35 mm.

A set of hulls is available for the leaching experiments and the metallographic studies. Leaching experiments can be carried out among a selection of four types of Zircaloy based alloys whose characteristics are summarized in Table 1.

The transportation of the samples from ATALANTE (CEA Marcoule) to the LECI hot laboratory (CEA Saclay) should be in late July 2014.

Table 1: Hulls irradiation characteristics.

Hulls reference	**COQ M5**	**MOX D4**	**COQ UOX2**	**COQ UOX3**
Cladding material	M5	Inner layer = Zircaloy 4 Outer layer= Zr-0,8% Sn	Zircaloy 4	Zircaloy 4
Fuel type	UOx (3,88% ^{235}U)	MOX (7,2 % Pu)	UOx (3,7% ^{235}U)	UOx (3,7% ^{235}U)
Number of cycles	4 cycles	4 cycles	4 cycles	4 cycles
Mean burn-up	46570 MWd/t_{HM}	54500 MWd/t_{HM}	39700 MWd/t_{HM}	48200 MWd/t_{HM}
Reactor	EDF PWR 1300 (Nogent 2)	PWR Gösgen (Switzerland)	EDF PWR 900 (Chinon B1)	EDF PWR 900 (Cruas 4)
Discharged from the reactor	June 2004	2002	March 1992	1994
Discharged from the hull rinser (La Hague)	October 2009	September 2008	August 1999	June 2004
Arrival in Marcoule (CEA)	2010	2009	1999	July 2004
Number of samples	4	4	4	4

The physical appearance of the selected hulls is shown in Figure 2. The shape of the hulls deviates from a perfect cylinder. We will have to take into account this shape to design a specific sample holder for the leaching experiments.

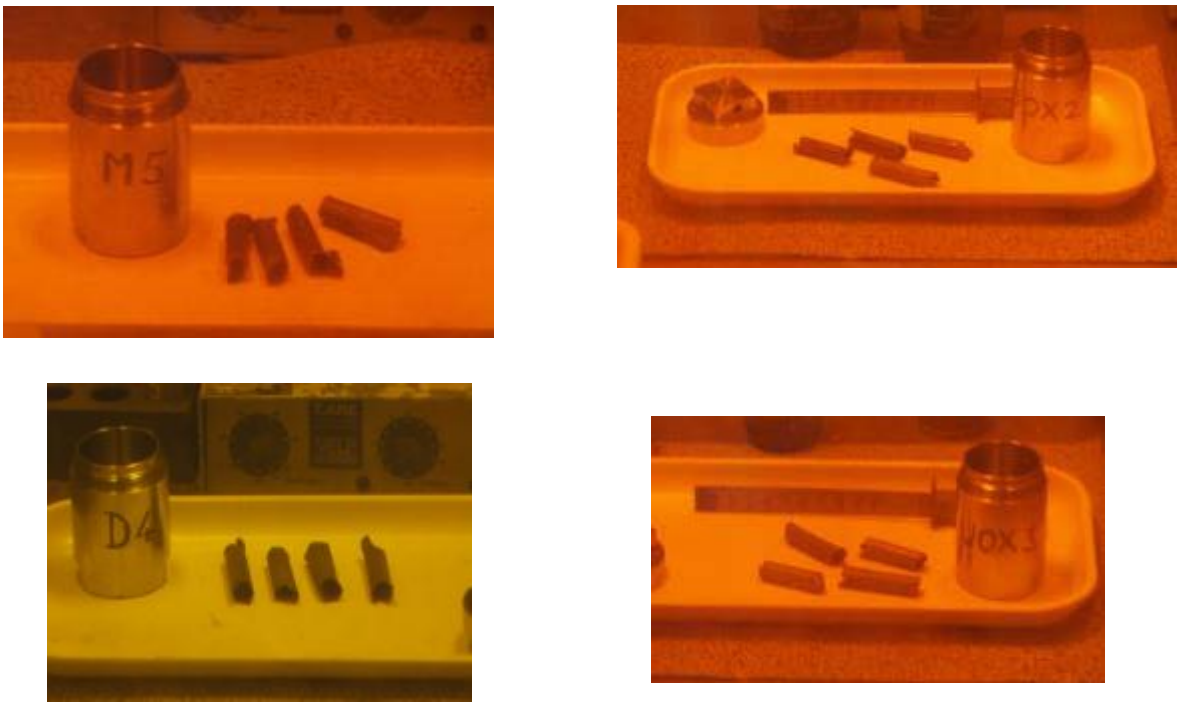

Figure 2: Photograph (taken through a cell window) of the sheared cladding.

1.2 Description of the leaching experiments

1.2.1 Description of the hot cell

Leach tests will be conducted in the I1 shielded cell at the LECI hot lab[1]. The cell I1 contains two main pieces of equipment (Figure 3): a X-ray Radiography bench and a laser welding machine.

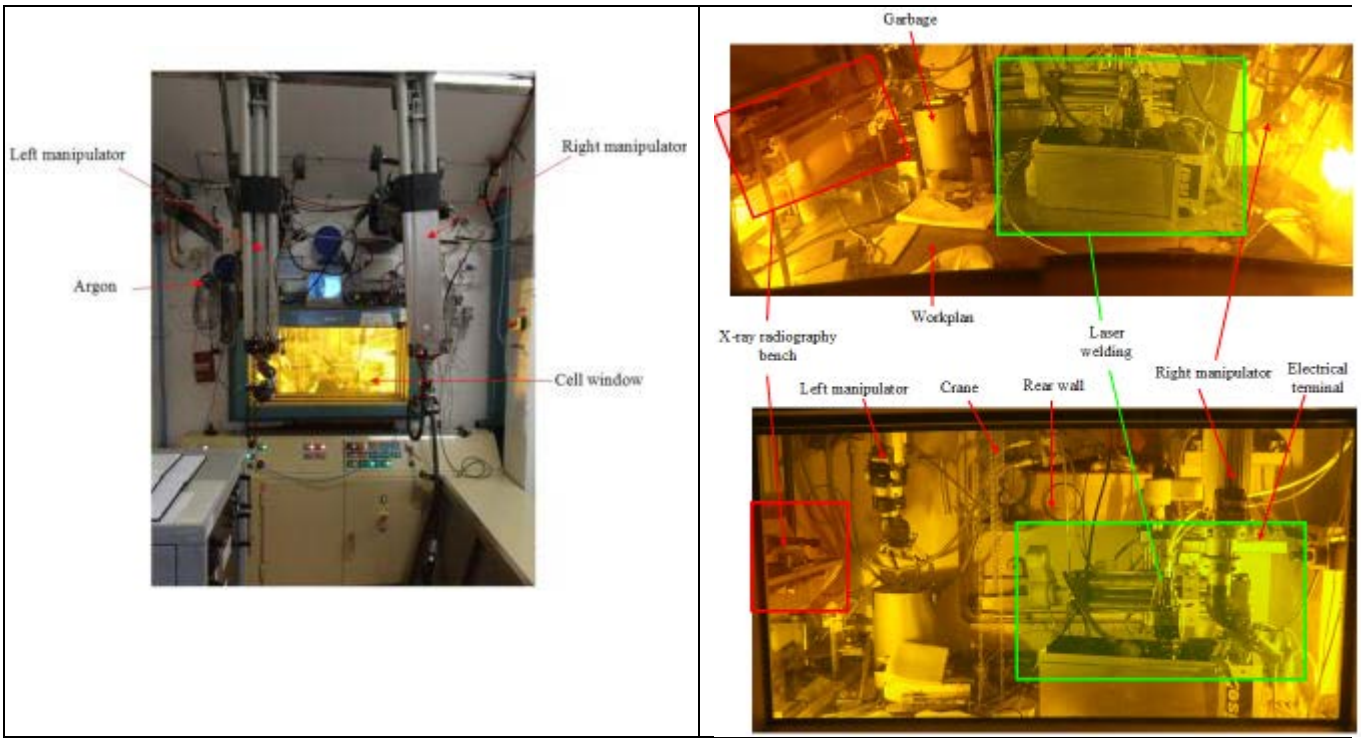

Figure 3 : Front view and interior of the I1 hot cell.

As the leaching experiments are a new technique for our hot lab, some parts of the hot cell and the safety procedures (handling of alkaline solution, acid, way out of the solution samples by the roof of the cell…) will be modified. For example, we must reorganize a part of the cell to place the leaching pots in the bottom of the cell (Figure 4). Four leaching experiments can be carried out in the hot cell (including one reference).

The introduction of new equipment (scale, gas hose, gas connectors, vials, titanium pots, stainless steel accessories…) must be implemented. And a protocol for the transfer of solution samples from the LECI to the chemical analysis laboratory must be defined.

[1] LECI, HOT CELL LABORATORY, CEA, Saclay (France).
http://materials.extra.cea.fr/en/PDF/LECIWaferCEA2012UK_12MD.pdf

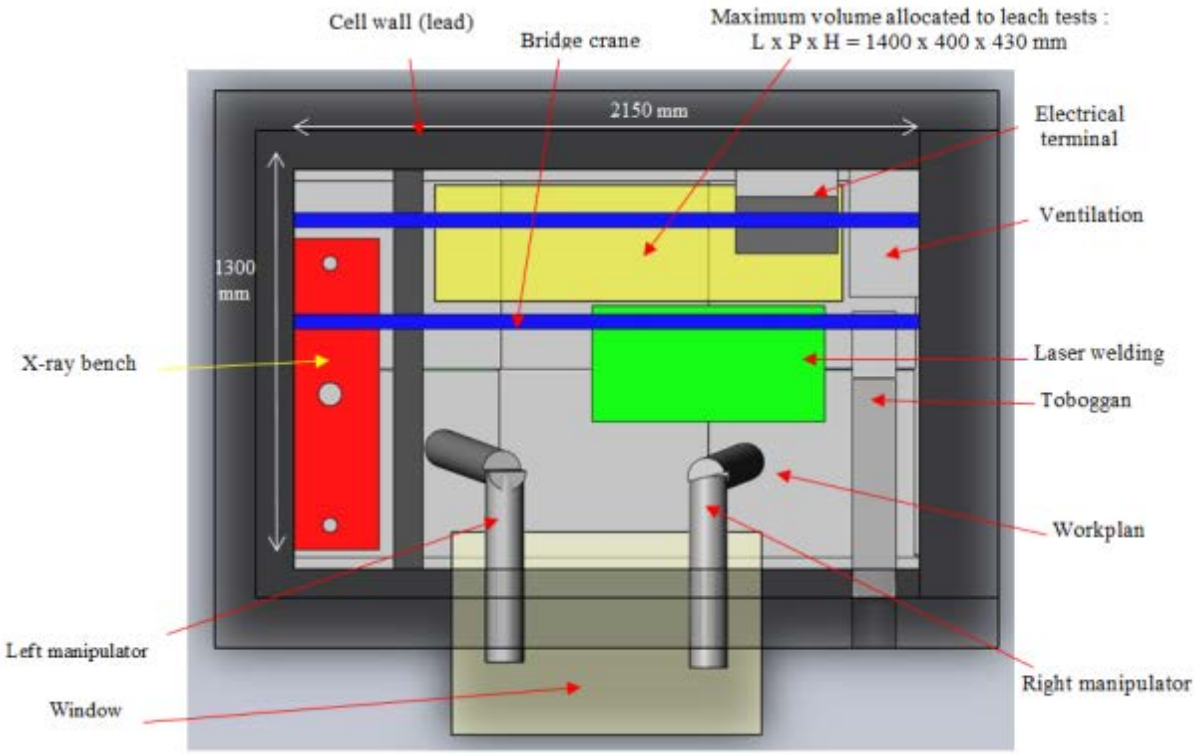

Figure 4: Schematic top view of the I1 hot cell.

1.2.2 Experimental conditions

^{14}C releases under aqueous dissolution conditions will be studied. Leach tests will be conducted in the shielded cell at room temperature (~ 25 °C) with synthetic cementitious groundwater in static mode (without solution renewal, initial volume from 200 to 300 ml).
The test specimens (~35 mm segments of clad rods) will be introduced into sealed titanium (and stainless steel) leaching pots containing groundwater for leaching tests.

An alkaline solution of deionized water and Portlandite $Ca(OH)_2$ ([Ca] = (20 ± 1).10^{-3} mol/l) is chosen as leachant. The pH is about 12.4. To have an anoxic atmosphere the solution will be sparged with Argon at least 3 h before initiating the leaching tests. Solution samples will be taken over a period of 12 months at the following intervals: 14, 90, 180 and 360 days. The volume of each solution sample will be about 15 ml collected in plastic vials. The vials will be manually released from the hot cell (through the roof). Outside the hot cell the solution samples will be decanted into clean glass vials and transferred to another hot lab for the chemical analysis.

For each reactor, two hulls will be inserted in the titanium sample holder.

The sample holder and the hulls will be separated by a ceramic liner to avoid galvanic corrosion (Figure 5).

At the end of each experiment the leaching vessel will be opened. The sample holder, the samples, the sampling rods and the vessel walls will be rinsed but the procedure is not set yet.

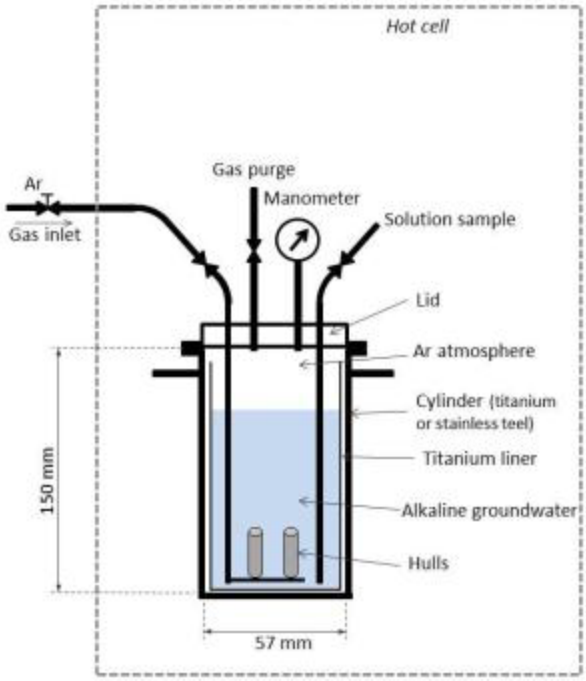

Figure 5 : Schematic description of experimental setup for static leaching tests.

1.2.3 Experimental setup

Since the handling of the leaching equipment has to be performed with manipulators: a specific experimental design was chosen. This design is derived from one already used in CEA Marcoule (DEN/DTCD/SECM/Radioactive materials and vitrification processes laboratory).

The experiments will be carried out in sealed metallic reactors (total volume approx. 385 ml) (Figure 6), with three valves in the lid to allow sampling of solutions, gas purge and to adjust the pressure with Argon gas during the experiment. The sealing valves are designed for remote use.

The leaching vessel is in titanium, fitted with a titanium liner to contain the solution. On both the liner and titanium sample holder, a passivated TiO_2 film will be formed to ensure no interaction between the species generated by water radiolysis and the experimental setup. The rods

(tubing), liner, sample holder and the lid will be made of titanium. The other metallic parts are made of stainless steel.

An argon atmosphere within the reactor (3.5 bar) will ensure the anoxic conditions. The leachant will not be refilled during this static leaching phase. It will be mixed thanks to argon bubbling.

The sample holder will also be immersed in the alkaline solution.

As it is foreseen, a maximum of four leaching reactors is possible in the hot cell. The leaching experiments will be performed on three different types of Zircaloy-based hulls to keep one reactor as a reference for the chemical analysis. The samples will be: 2 MOX hulls, 2 M5 hulls and (optionally) 2 Zy-4 (UOX3 or UOX4).

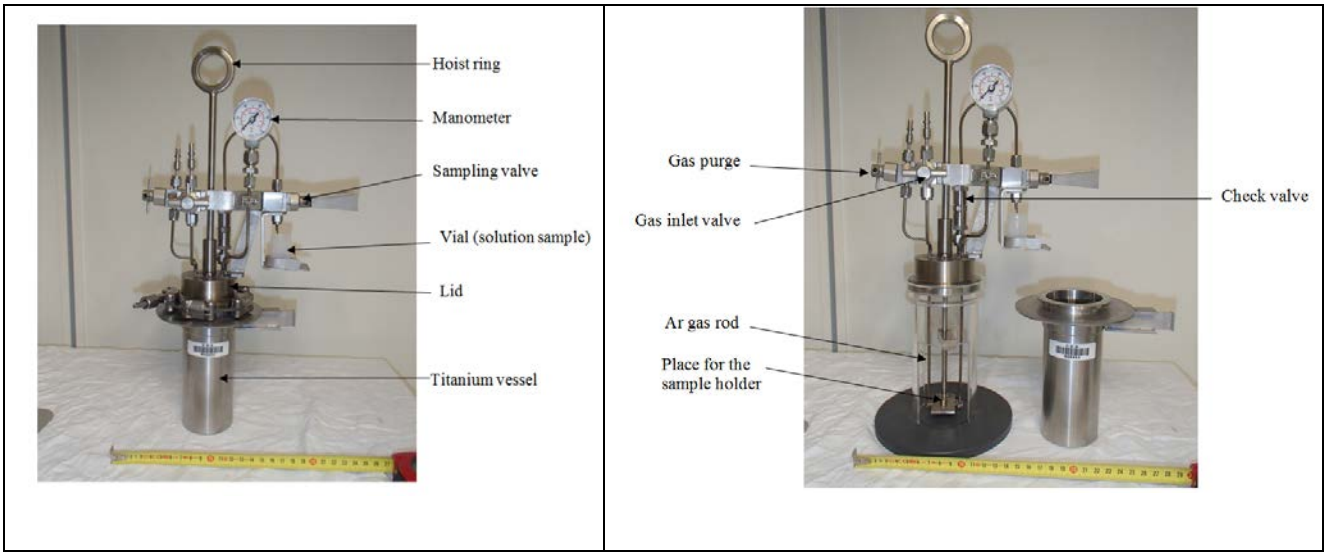

Figure 6 : Overall view of the leaching reactor (open and closed).

Planning

- ➔ A sample holder has still to be developed. The experimental setup will be manufactured by the end of 2014.
- ➔ As the leaching experiment is a new technique at the LECI hot laboratory, a nuclear safety report has to be prepared and should be finished by the end of 2014. This safety report will describe the leaching experiments, the new equipment introduced in the hot cell, the way out and transportation procedure of the liquid samples.
- ➔ A feasibility study will be made for the gas sampling.

➔ A risk analysis will be assessed and a specific authorization is needed from the nuclear safety authority before starting the leaching experiments.

Acknowledgments

The authors gratefully acknowledge the contributions of AREVA-NC and G. Ferlay (CEA, Marcoule, DEN/DRCP/SERA/Laboratory of dissolution studies) for providing the hulls and V. Broudic-Oliver (CEA Marcoule, DEN/DTCD/SECM/Radioactive materials and vitrification processes laboratory) for the technical details about the leaching experiments.

2 Definition of operating conditions at INR

2.1 CANDU fuel characteristics

In the frame of CAST project, INR proposed to measure both the total C-14 in CANDU spent fuel (including its partition between organic and inorganic species) and to perform long-term corrosion tests on un-irradiated Zircaloy-4 and irradiated Zircaloy-4 sampled from a spent fuel element from Cernavoda NPP. The experiments will be performed in conditions simulating cementitious environments. In this report the leaching test is described. The corrosion experiments are described in detail in the D3.4.

Two CANDU units are currently in operation at Cernavoda NPP; U1 is in operation since December 1996 and U2 is in operation since November 2007. The core of the two units consists of 380 fuel channels with 12 fuel assembly on each channel.

CANDU fuel assembly contains 37 elements comprising of sintered UO_2 pellets (natural uranium) in Zy-4 tubes. The 37 elements are circularly arranged in three rings of 18, 12 and 6 elements respectively, around a central element (Figure 7).

Figure 7 : CANDU fuel bundle.

CANDU units are designed to load and unload their fuel continuously at full power by disconnecting individual pressure tubes. The average loading/unloading rate at Cernavoda NPP is around 16 FA/day, that means in 30 years of operation (although it is proposed to refurbish the units to extend their life to 40 years) the units U1&2 of Cernavoda NPP will generate around 3.5E+05 FA.

Each CANDU FA contains around 4.2 kg of Zy-4 (fuel claddings, end-caps, end support plate, inter element spacers and pads). This means that around 1.5E+06 kg of Zy-4 will be disposed of in the geological repository.

The main design parameters for CANDU spent fuel are summarized in Table 2.

Table 2 : Design parameters for CANDU spent fuel assembly.

Parameter	Value
FA dimensions: diameter (mm) length (mm)	 102 495
Nominal mass (kg)	23.7
U mass (kg)	18.9
Average burn-up (MWday/t U)	7500

The irradiated Zy-4 samples that will be used in the experimental programme developed by INR under CAST-WP 3 will be sampled from an irradiated fuel bundle that was irradiated in the CANDU-Unit 1 for 1 year and kept for cooling 4 more years in the Spent Fuel cooling bay. After the cooling period, the fuel bundle was transported to RATEN-ICN for different investigations and in the last year it was in the INR hot cells. The protocol for cutting the hulls needed for the corrosion/leaching tests that will be performed under the CAST-WP3 was approved and the hulls have to be cut and the spent fuel to be dissolved using nitric acid. SEM investigations on the CANDU spent fuel were already performed and the Zy oxide layer measured along the fuel tube is between 3 µm and 3.5 µm. Real measurements for nitrogen content of the Zy-4 are available.

2.2 Leaching test

Un-irradiated (oxidized and non-oxidized Zy-4) and irradiated Zy-4 samples of known dimensions will be immersed for long periods in anoxic alkaline environment (solution saturated in $Ca(OH)_2$ at pH12.5, at both, room temperature and 80°C), and after different intervals of immersion polarization scans will be performed (see D3.4 report for details on the corrosion measurements).

Samples collected from $Ca(OH)_2$ solutions from both the long tests and from the corrosion test will be analysed for C-14 measurements.

3 Definition of operating conditions and presentation of the experiments at SCK•CEN

3.1 Zircaloy samples at SCK•CEN

SCK•CEN has at its disposal both non irradiated and irradiated Zircaloy samples (Zircaloy-2/4 and M5™, which is the current reference cladding for AREVA fuel). The irradiated materials are representative for end-of-life conditions in nuclear power plants and thus offer the advantage of a realistic input of ^{14}C release into the national safety cases (WP6).

At the moment of drafting this report (04/07/2014) the approval of using M5™ material from AREVA was missing. For this reason no preliminary experiments have been performed on this material, but only on Zircaloy-4. These Zircaloy-4 specimens from two Belgian nuclear reactors (Tihange and Doel) are ready for gamma ray spectrometry analysis.

The initial chemical composition of the SCK•CEN samples is available in their material quality control certificate. The chemical composition of a non-irradiated Zircaloy specimen is detailed in Table 3.

Table 3 : Specification chemical composition of a non-irradiated Zry-4 specimen available at SCK•CEN*.

wt %			ppm						
Sn	Cr	Fe	C	Hf	Si	W	O	N	Zr
1.2-1.7	0.07-0.13	0.18-0.24	270	100	120	100	1000-1400	< **50**	Bal.

**Reference: Material quality control certificate.*

A non-irradiated Zircaloy specimen is depicted on Figure 8.

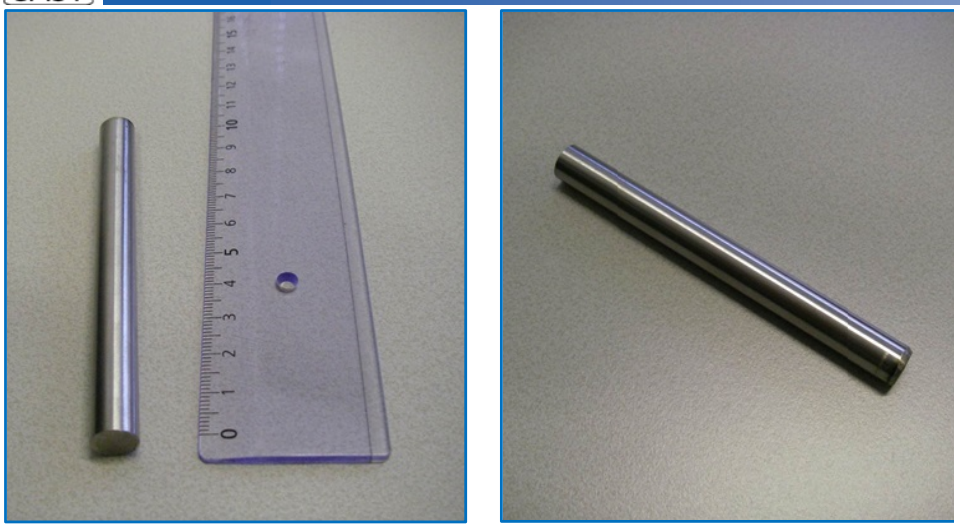

Figure 8 : A non-irradiated Zry-4 specimen before cutting.

The burnup of the candidate CAST specimens has been estimated between 50-60 MWd/kgHM based on the reactor power history and the calculated power mapping across the core. More accurate burnup data will be presented after having more details on the irradiation history and campaign. The dose rate at different distances is measured for two Zircaloy specimens and the values are presented in Table 4.

Table 4 : Dose rate from irradiated Zircaloy samples at 10 cm distance (measured on 01/07/2014 with Automess 6150 AD5 counter).

Sample code	at 10cm
D05	10 mSv/h
E14	3.5 mSv/h

3.2 Description of the experiments

Static and accelerated corrosion tests are planned. Therefore two different setups were drafted. A theoretical description of the setup is detailed below and two experimental cells are drafted for static and accelerated leaching tests. Both test setups have to be placed either in a hot cell or glove box depending on the surface dose rate of the Zircaloy specimens. The atmosphere in the test cell has to be oxygen free, for this reason the hot cell/glove box itself should be also under anoxic atmosphere if technically possible. In the hot cell technical adjustments are necessary to maintain anoxic atmosphere. During the experiment an anoxic atmosphere will be maintained by continuous flow of argon, and the oxygen level will be monitored. The gas tightness of the test cells will be checked before starting the experiments. These measures help us to reduce the risk of having oxygen inside the test cells even when there is a leak of the cell.

Leaching experiments will be done in an airtight small volume (≤ 100 cm^3) container with possibilities for sampling without opening the vials. The cell will be equipped with a gas inlet for the purging gas (argon), a gas outlet for the gas chromatography (GC) system and an outlet for the liquid phase sampling which is connected to a GC or ion chromatography (e.g. HPLC) unit.

Experiments were planned at two different temperatures. One experiment was planned at ambient temperature (T= 20-30°C) and another at a higher temperature of 80°C to mimic the heat evolution during the first phase of the nuclear waste storage. However, in the long term safety case the most representative temperature is estimated to be between 20-30°C (KUR et al. 2009; WEE et al. 2013), therefore temperature within this range will be applied for our experiments.

The following pore water is planned to be used for the leaching/corrosion tests: de-gassed $Ca(OH)_2$ (pH ~12.5). The pore water will be prepared in a glove box under anaerobic conditions and degassed with (nitrogen or argon) to reduce the risk of any traces of environmental origin $^{14}CO_2$ absorbed in the solution.

3.2.1 Static leaching test

Before starting the experiment the glove box/hot cell will be flushed with argon to exclude oxygen from the system, eventually obtaining anaerobic condition. During the static leaching test, irradiated samples (approximately 0.5 cm thick) will be placed in a test cell filled with saturated Portlandite electrolyte. It has to be noted that the mode of sample introduction is not fixed yet. The easiest way of sample introduction is to place the sample at the bottom of the vial but then not the whole surface is in contact with the pore water. Another option could be to place the sample in a chemically resistant sample holder and immerse them together into the solution. The cell will be closed gas tight with a screw cap having two outlets, one for gas sampling and another for liquid sampling (Figure 9)**.** The temperature of the cell is kept at a previously determined optimal temperature (either ambient temperature or 80°C to simulate the heat evolution due to radioactive decay in the waste container). Sampling will be done from the gas and liquid phase just at the end of the leaching test duration. The leaching test will last one year as recommended during the CAST Work Package 2&3 meeting in Paris. The carbon components are accumulated in the test cell and transferred to the analytical instrument through their corresponding outlets.

For the static leaching test one cell will be used for the frequent sampling and the other cells won't be disturbed during the experimental period. The sampling frequency will be defined later in a common project work package document. From the undisturbed cells sampling will be done only once at the end of the experiment.

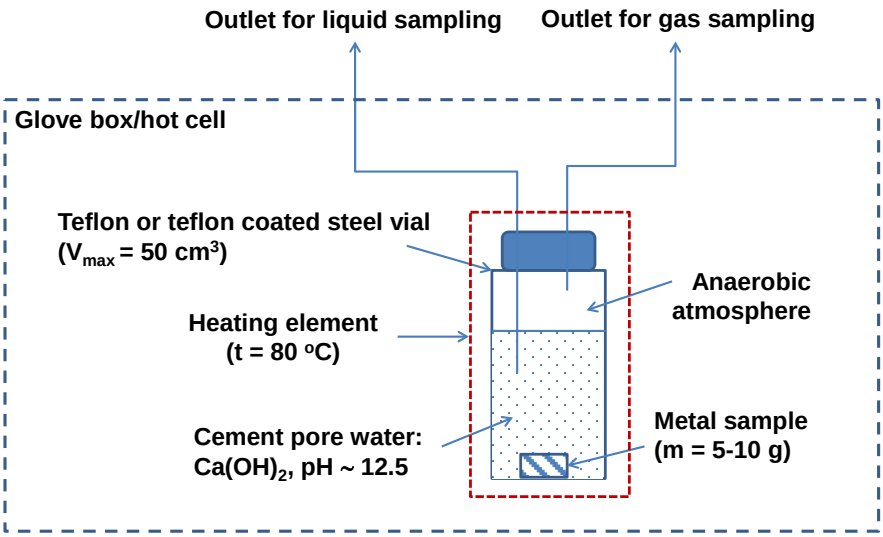

Figure 9 : Proposed layout of the static leaching test setup in an autoclave in glove box under reducing atmosphere.

3.2.2 Accelerated leaching test

The accelerated leaching tests are accelerated corrosion tests. They are described in detail in the D3.4. Globally, they consist of imposing a pre-determined potential to the samples that would result in accelerated active corrosion of the sample.

The metal samples are first polished and then either embedded in a radiation resistant resin or just simply immersed into the electrolyte after point welding a wire to the back of the sample which serves as an electric connection (Figure 10). Silver reference and platinum counter electrodes will be used. The electrodes will be introduced through the cell cap but these holes will be made gas tight by adding resin or glue into them. The experiment will be stopped after dissolving sufficiently enough material. For the accelerated leaching test, one sample will be taken at the end of the experiment. After disassembling of the test cell, another sampling will be done and the liquid and solid radioactive waste will be collected separately.

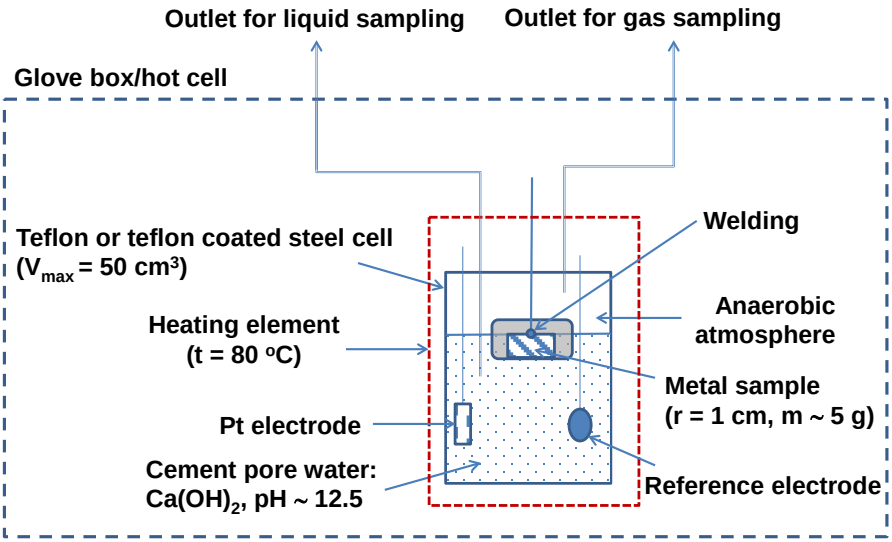

Figure 10 : Proposed layout of the accelerated leaching test setup in an autoclave in a glove box under reducing atmosphere.

4 Definition of operating conditions and presentation of the experiments at RWMC

4.1 Irradiated BWR Zircaloy cladding (YAM et al. 2013)

4.1.1 Sample pretreatment

Irradiated Zry-2 claddings from a BWR were used for the tests. The features of the specimens are shown in Table 5. The claddings were cut to heights of 2 cm for the leaching tests. The pretreatment procedure is shown in Figure 11. First, bonding fuel elements were removed by mechanical drilling. After that, reprocessing steps were initiated and fuel dissolution processing was carried out with 4 N boiling nitric acid for 4 hours. After fuel dissolution processing, the specimens were cleaned ultrasonically with pure water. Underwater polishing with a diamond file was carried out in the order of #150 and #800 grits to remove oxide films on the inside and outside surfaces and expose the base material. A picture of specimen before polishing is shown in Figure 12.

Table 5 : Feature of specimens before pretreatment.

Fuel Type	Reactor Type	Materials	Nitrogen conc.	Burnup (GWd/t)	Cycles	Outer oxide film thickness (average, μm)
STEP3	BWR	Zry-2	Not opened	39.7	3	4.7

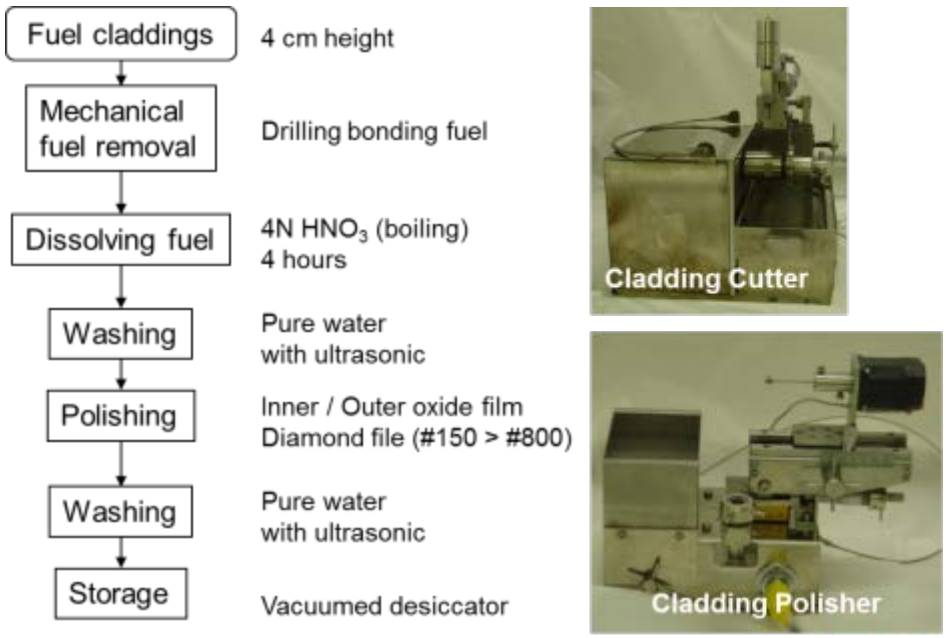

Figure 11 : Pretreatment for specimens.

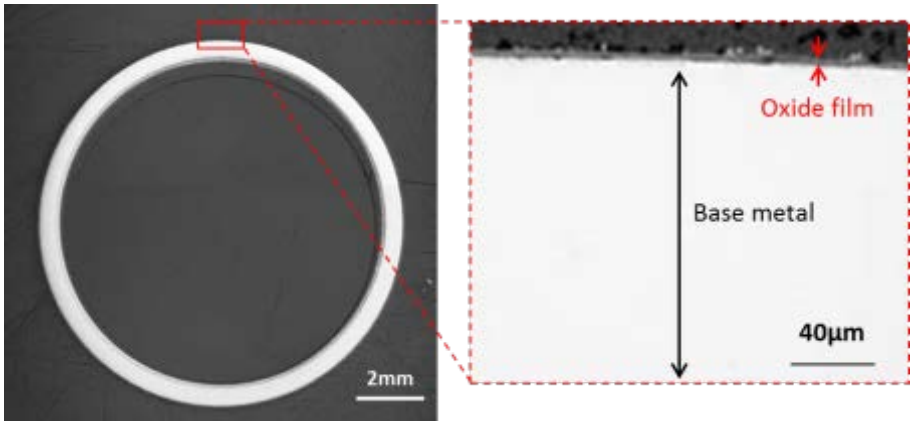

Figure 12 : Picture of specimen before polishing.

4.1.2 Leaching experiment setup

Since it is necessary to maintain the atmosphere for a long period of time, the container shown in Figure 13 was used. In order to avoid contact of the specimen with different metals, a glass vial was used for immersion as an inner container. Furthermore, to prevent release of C-14 from the inner container in the event of generation of gas containing C-14, an outer container made from stainless steel was prepared. A gas sampling line was not installed in the outer container in order to maintain prolonged sealing performance. Therefore, at the time of sampling, the inner and outer containers were opened within a simple glove box or a glove bag for collecting C-14 in the gaseous phase. The outer container was sealed with bolts using a silver-plated stainless steel gasket. A preliminary leak test using helium was carried out in advance, and after confirming that the stainless steel container was properly sealed, it was used for the leaching test.

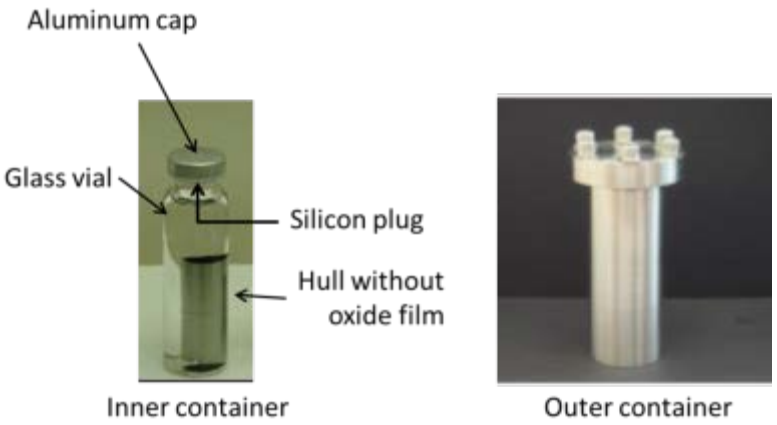

Figure 13 : Pictures of the test containers.

4.1.3 Experimental conditions

Experimental condition of leaching test was shown in Table 6. A NaOH solution adjusted to pH 12.5 was used for the test solution. Although it is possible for a saturated solution of $Ca(OH)_2$ to exist in an actual disposal environment due to the presence of cement material, only the pH was limitated in order to avoid the generation of $CaCO_3$ precipitates. N_2 and H_2 gases were bubbled in the test solution just before the specimen was immersed, which reduced the oxidation/reduction potential to less than -250 mV. Immersion was carried out within a simple glove box containing N_2 so that there was a nitrogen atmosphere within the immersion container.

Table 6 : Experimental condition of leaching test.

Sample	Hull without oxide film
Solution	Degassed NaOH (pH 12.5, Eh < -250 mV)
Temperature	Room temperature (about 25°C)
Container seal	Sealed after N_2 gas purge
Test period	0.5, 0.75, 1, 2, 3, 5, 7, 10 years 3~10 years; plan (immersion is started)

5 Definition of operating conditions and presentation of the experiments at JRC-ITU

5.1 LWR Zircaloy cladding

The test material is standard Zry-4 from a high burn-up LWR fuel.

There is no further information for the claddings other than the manufacturer's specifications (Table 7). For impurity levels (eg. C, N, O) can be taken if necessary. ITU will use a standard specification value of Zircaloy 4 if no other value is available (e.g. 80 ppm N for Zry-4). If a value measured for a similar fuel is available this could be used.

For stainless steel cladding, cladding from a fast reactor fuel project NIMPHE 1 & 2 will be used. These were 25%Pu-U nitride and carbide fuels that were irradiated in the Phenix reactor. Metallography of the cladding of the selected NIMPHE 2 carbide fuel of approximately 55GWd/tHM burn-up is available.

Some metallography of NIMPHE 2 cladding is available.

Table 7 : Main elements in Zircaloy-4 (ATI-Wah-Chang production specifications).

Element	Content (wt%)
Zr (Hf)	97.56-98.27 (Hf<0.01)
Sn	1.20-1.70
Fe +Cr	0.28-0.37
Fe	0.18-0.24
Ni	<0.007
C	<0.027
N	<0.008
H	<0.0025
O	-

Total burn-up (probably local BU) and irradiation data will be available for the high burn-up fuel and Zircaloy 4 cladding.

C-14 content could be estimated from the burn-up and C, N specification limits. It is very unlikely that measurements are available.

Samples will be cut as 5mm long rings:

a) Some samples will be cut at fuel height: they will need fuel removing but they will present higher burn-up/C-14 content,

b) Further samples will be cut from above fuel height which are clean but then have a lower irradiation and C-14 content.

One sample will be mounted for metallography, another will be used for total C content determination. The remainder will go for leach testing in the autoclave. Any excess samples will be retained for future repeat testing

5.2 Description of the leaching experiments

5.2.1 Sample preparation

If from fuel height, then the ring samples will be cleaned by placing in 7M HNO_3 (for ~3h at room temperature) then they will be washed and cleaned ultrasonically in successive stages with distilled water (two times) and then alcohol.

If samples are from above fuel height then there will be only a short or no acid cleaning (dependent on contamination), thereafter just ultrasonic cleaning with water (two times) and then alcohol.

5.2.2 Leaching Test Autoclave

The leach tests will be carried out in a Berghof autoclave (Figure 14) with a Teflon lining of 150ml volume using 100 ml solution with the 5mm ring samples of irradiated cladding, placed on a quartz sample holder to maintain the sample in the middle of the solution and away from the liner walls (reduce local dose rate). The autoclave has a heating mantle in order to maintain the temperature at 80°C or at 30°C (only for Zircaloy) (Figure 14).

After purging solution and gas volume with a reducing gas to remove oxygen (eg Ar-6.5% H_2) then the sample will be heated and left for the standard time of 3 months before stopping the heating and beginning the analysis.

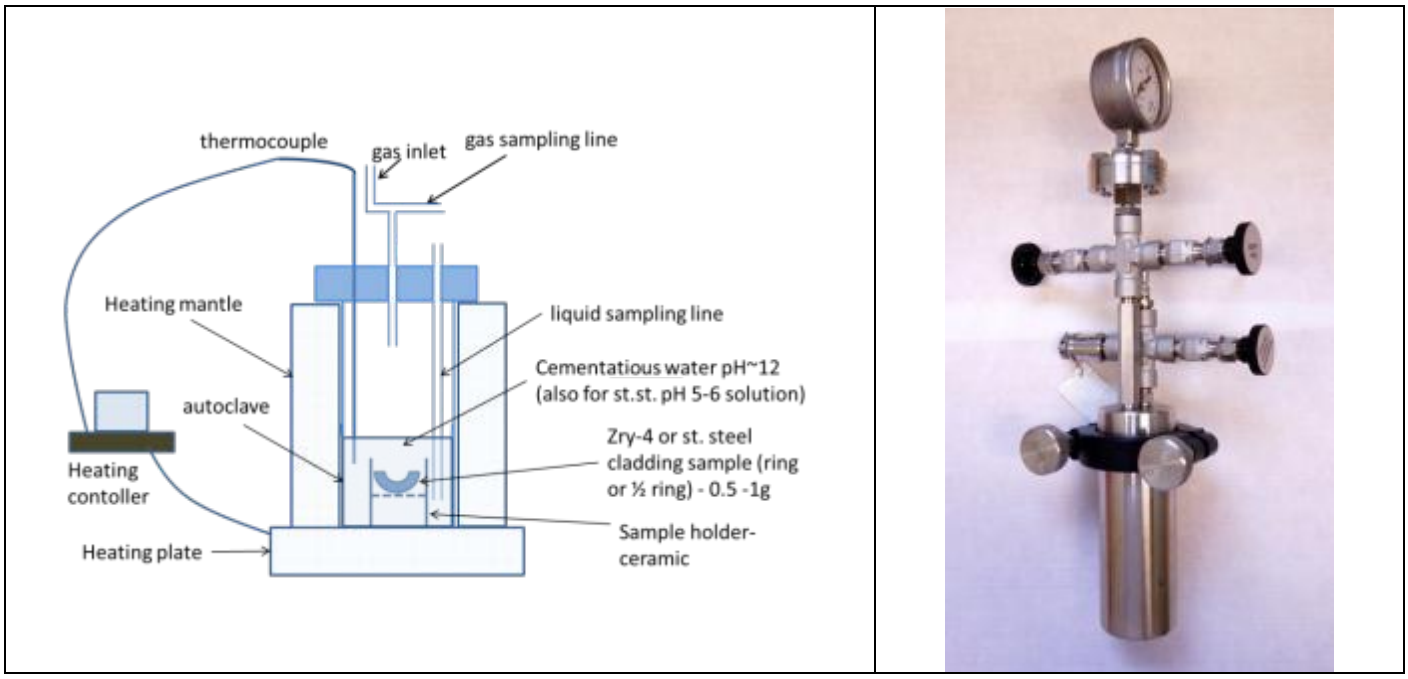

Figure 14 : Schematic diagram of the autoclave set-up and picture of the autoclave (with Teflon lining).

5.3 Experimental conditions

Commercial buffers (pH 11 is a HBO_2/KCl/NaOH buffer and pH 12 is a K_3PO_4 buffer) were discarded in place of simpler solutions such as $Ca(OH)_2$ at pH 12 representing cementitious waters, even if they are not so stable.

Note: pH accuracy drops at extreme pH's (both high and low).

Proposal to use anoxic conditions (pO_2 ~1ppm) by use of high purity N_2 or Ar flow, since this seems the most likely conditions in closed or non-surface repositories.

The initial temperature of 90°C was proposed; this will be revised to 80°C to match that of RWMC & SCK-CEN Mol.

A slight overpressure of 1-2 bar will be used to help extraction of gas or liquid samples from the autoclave. There was little interest to examine pressure variation.

The sampling strategy will be as simple as possible.
This limits the handling and risk of contamination in hot cell and increases the total C-14 (as organic or CO_2/CO_3^-) in the samples and aids analysis. The samples will be extracted directly from the autoclave at the end of the test. One intermediate sampling of gas and of liquid phases from the autoclave is possible but tests with no intermediate sampling are strongly preferred.

6 References

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